MELCOR further development in the area of air ingress and the effect of nitriding

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ABSTRACT

The MELCOR code developed at Sandia National Laboratories (SNL) for the USNRC is used in Switzerland for analysis of severe accidents in light water reactors. In order to address air ingress during reactor and spent fuel scenarios, a new oxidation model was developed at PSI to capture the accelerated (breakaway) oxidation in air. In this model the nitrogen is not treated as an active species but as a catalyst. Implementation into MELCOR and assessment of the model was the subject of previous ENSI-supported work at PSI. The work at PSI included participation in the OECD Sandia Fuel Project (SFP), in which two experiments were performed to simulate full-scale fuel assembly heat up and ignition in a dried-out storage pond, under «hot neighbour» and «cold neighbour» distribution of assemblies. Benchmark studies by the project participants were carried out for each experiment to assess the different models for air oxidation.

Application of the model to spent fuel uncovery sequences based on Fukushima Daiichi Unit-4 showed that ignition may occur due to the strong effect of nitrogen in promoting the oxidation in steam, especially if high rated fuel assemblies are grouped together (hot neighbour arrangement). Even if ignition does not occur, as may be the case with a cold neighbour arrangement, complete oxidation of the cladding in a steam-nitrogen environment would be expected after about a week following transition to breakaway oxidation, compared with several weeks without breakaway.

The present project addresses a model limitation in that nitrogen is not treated as a chemically active species. An outcome of SFP and a recent QUENCH experiment is that during air ingress the cladding readily reacts with nitrogen to from zirconium nitride at locations where the oxygen has been fully consumed. To address this behaviour a PhD project has recently been launched. Two major sources of difficulty make this task challenging, notably the complex chemical interactions when nitrogen and oxidation are reacting together with the partially oxidised cladding, and the sensitivity of the nitride formation to the existing stoichiometry of the Zr(N,O). The study has begun with a review of current knowledge of the phenomenology.

Project goals

Following a national research programme investigating the behaviour of BWR spent fuel under total loss of coolant conditions [1] the US NRC together with the NEA-OECD conducted an international programme to investigate the behaviour of prototypical PWR spent fuel under similar conditions. The spent fuel experiments also revealed strong nitriding behaviour under oxygen starvation, followed by re-oxidation of the nitride when oxygen is again present later. These phenomena motivate the development of model for the reactions involving nitrogen and nitride. Investigation of nitride formation has recently begun, with the objective of developing a model for nitride formation.

In addition, the events at the Fukushima Daiichi station, especially the accident of unit-4, underlined the need for further investigation of spent fuel behaviour under long term loss of cooling and also a continued improvement in our understanding of severe accident behaviour and of the modelling tools used for accident analysis.

In parallel, PSI developed a new oxidation model to capture the accelerated oxidation that is observed to occur in air, and also in steam at low to moderate superheating characteristic of spent fuel uncovery conditions. At present the model does not represent the role of nitrogen except as a catalyst for oxidation by oxygen or steam, and hence does not capture the observed nitride formation. The existing PSI model provides a launchpad for development of a model for zirconium nitride formation.

The goals of the present project are:

To acquire knowledge of the reactions of zirconium-based cladding in mixtures of steam and/or oxygen with nitrogen for a wide range of conditions and initial oxidation state.

To extend the existing air oxidation model to include reactions with nitrogen in a sufficiently general way to cover all likely transient conditions.

Work carried out and results obtained

OECD SFP Project

The OECD SFP project continued until February 2013 with the successful completion of the benchmark study on Phase 2 and the final seminar on 22nd and 23rd of October 2013. PSI participated in the benchmark with simulation using MELCOR in which the PSI oxidation model was implemented. Phase 2 provided an opportunity to study the cold neighbour fuel assembly arrangement in (comparison with Phase 1 hot neighbour) and to address the lateral spreading of the zirconium fire from high temperature to lower temperature areas, thus extending the assessment base for the severe accident codes – ASTEC, ATHLET-CD, MELCOR were used in the study [2], [3].

The outcome of the benchmark was that all the codes described the experiments well until ignition of the zirconium fire, after which the results diverged both code-code and user-user. The SFP configuration and transient conditions lie outside those for which the codes were originally designed, requiring very particular guidelines to represent the processes adequately within the scope of the code models. Examples are the lateral radiation between fuel assemblies of very different power ratings that led to the large temperature gradients observed in phase 2, and the racks separating the assemblies which are specific to SFP and not part of any reactor configuration The MELCOR simulations were representative of other codes; the PSI analyses were previously described. Also – except ATHLET-CD – there is no model of nitriding. Separate effect tests are needed to provide an adequate data base for the development of such a model.

The experimental results were used to assess the PSI air oxidation and breakaway model developed for the implementation in SCDAPSim and MELCOR and compare its results with the Sandia model for breakaway in an air environment. As well as implementation in a local version of MELCOR 1.8.6 YV 3084, a special version of MELCOR 2.1 (5101) also includes the PSI model [4]. Additional sensitivity options for breakaway in the PSI oxidation model have been also implemented to address remaining uncertainties [5]. Assessment studies using the data of the SFP project, QUENCH and PARAMETER data are ongoing.

Using the thermal hydraulic boundary data received from the SFP project several calculations were executed to investigate the behaviour of spent fuel stored in different ways like hot neighbour and cold neighbour storage (Fig. 1).

In Fig. 2 the time of ignition is shown for this two storage types and it can be seen, that the heat sink in the cold neighbour storage drastically reduces the danger of ignition of the cladding of the spent fuel. However, the oxidation continues below ignition temperature with kinetics following a linear

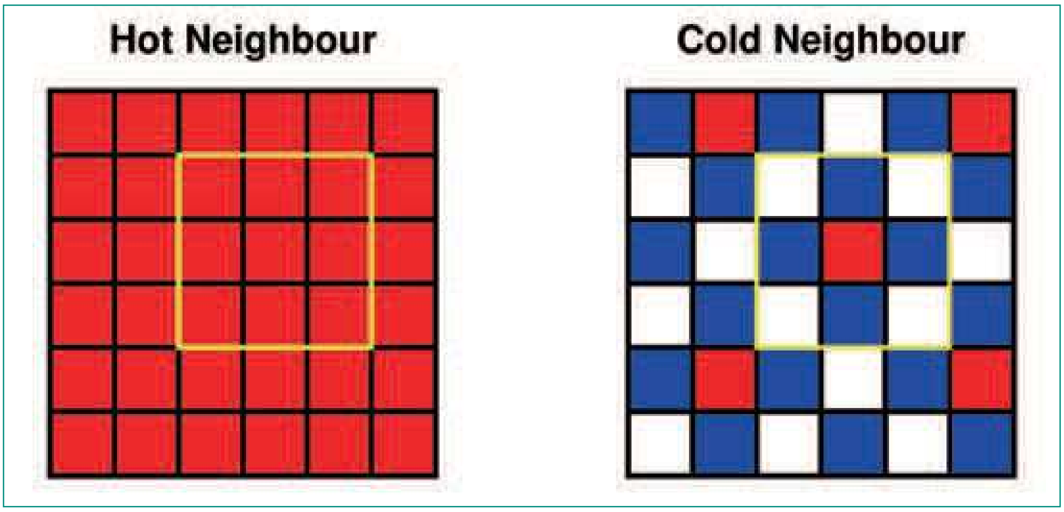

Fig. 1: *Hot neighbour and cold neighbour spent fuel storage according SFP experiments in phase I and phase II.*

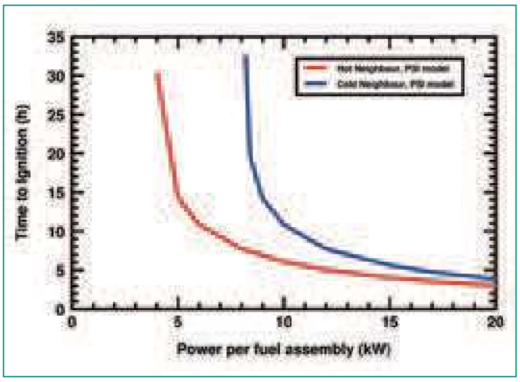

Fig. 2:*Calculated time to ignition for different heat loads of spent fuel assemblies in air for hot and cold neighbour configuration.*

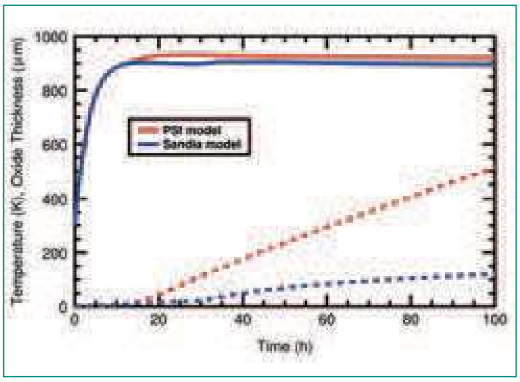

Fig. 3: *Oxide layer growth and peak cladding temperature with 8 kW heat load spent fuel bundle in cold neighbour configuration using PSI and Sandia breakaway model, not reaching ignition temperature.*

variation with time, such that integrity of the cladding will be lost due to complete oxidation within about one week (Fig. 3). This is in contrast to the parabolic kinetics adopted in the Sandia correlation which would not lead to complete oxidation even after several weeks [6].

Zirconium nitride modelling

Very recently, a PhD project has been launched at PSI, to develop a model for nitrogen reactions in an air or steam-nitrogen environment. The work has begun with a summary review of the basic principles, knowledge and sources of data [7].

Previously, many separate effect tests have been performed mainly at KIT and IRSN. Also, the integral tests were conducted in the frame of QUENCH-10 and -16. Through these air oxidation tests the nitride formation was observed under oxygen starvation and two major roles of nitrogen were identified.

The first role of nitrogen is the cladding degradation by forming a micro porous oxide scale due to the differences between the molar volumes of ZrN and ZrO_2. Through the pores by the ZrN inclusions in the oxide scale the oxygen could easily access and oxidizes the ZrN. During ZrN reoxidation ZrN is converted to ZrO_2 and hence oxide scale experiences the stresses due to the volume expansion and it leads to macro cracked oxide.

The second role of nitrogen is the exothermic heat release from the ZrN formation and reoxidation. The heat released from ZrN formation and reoxidation is same as the heat from oxidation by oxygen. Furthermore, a self-sustaining nitrogen-assisted degradation, $ZrN \rightarrow ZrO_2 \rightarrow ZrN \rightarrow \ldots \rightarrow ZrO_2$ would be likely to occur, following oxygen starvation conditions and subsequent reflood, which may have a large impact in the amount of hydrogen produced during reflood.

Currently some reactor system codes represent the nitrogen-driven cladding degradation as a catalyst effect by modelling the enhanced diffusion of oxidant and hence accelerated kinetics. However most reactor system codes do not implement ZrN formation heat release and none of them represents the ZrN reoxidation heat release.

The PhD is intended to address the most important knowledge gaps by means of a coupled experimental and analytical investigation. A first series of experiments will be performed in the beginning of 2014 under a range of thermal and oxidation states and prior histories. Analyses of the data will identify the dominant phenomena and hence provide the basis for a new oxidation/nitriding model. The model will be assessed using the data obtained, and the results will be used to specify conditions for further experiments and model refinement.

National Cooperation

The PhD project includes collaboration with ETH Zurich.

International Cooperation

The SFP project was organized by OECD-NEA with US NRC as operating agent.
The recently launched PhD project includes collaboration with Karlsruhe Institute of Technology.

Assessment 2013 and Perspectives for 2014

The SFP project provided a strong and extensive data base for code assessment in the area of spent fuel accidents. Important outcomes of the experiments were the importance of nitrogen as a chemical active species during air oxidation and a driver for the loss of structural integrity of the oxidised cladding. Simulation of SFP sequences indicate major concerns if fuel assemblies are exposed to steam-air or steam-nitrogen mixtures for more than a few days.
There is currently no model in MELCOR for the nitrogen chemistry. A PhD project has been launched at PSI to develop such a model to be implemented in the severe accident codes later.

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